Project 95061

Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides

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RESULTS TO DATE: Annual Progress Report

Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides

Project Number DE-FG02-05ER63979 July 2005

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Executive Summary

1. It has been determined that poorly crystalline CST and SNT prepared at low temperature (100-150 deg. C) exhibit much faster kinetics in uptake of Sr2+. 2. In-situ X-ray studies has shown that SNT is a precursor phase to the formation of CST. 3. It is possible to form mixtures of CST and SNT in a single reactant mix by control of temperature and time of reaction. 4. It has been found that addition of a small amount of Cs+ to the reactant mix for the preparation of Nb-CST allows formation of the crystals in one day rather than ten days at 200 deg. C. 5. These discoveries suggest that a proper mix of sorbents (SNT, CST, Nb-CST) can be made easily at low cost that would remove all the HLW at the Savannah River site with a single in-tank procedure. Research Objective The basic science goal in this project is to identify structure/affinity relationships for selected radionuclides and existing sorbents. The research will then apply this knowledge to the design and synthesis of sorbents that will exhibit increased cesium, strontium and actinide removal. The target problem focuses on the treatment of high-level nuclear wastes. The general approach can likewise be applied to non-radioactive separations.

Research Progress

During the past year of this project we have focused on the following research efforts (1) a comparison of poorly crystalline CST with the highly crystalline CST for Cs+ and Sr2+ uptake (2) improving the kinetics of strontium and actinide uptake of SNT, sodium nonatitanate (Na4Ti9O20.xH2O). (3) a continuation of our in situ studies into the mechanism of uptake of Cs+ and Sr2+ by CST and (4) continued collaboration on the theoretical aspects of CST exchange mechanism in collaboration with the Notre Dame University team.

Experimental Results

The SNT phase or sodium nonatitanate is a getter for Sr2+ and some actinides, Pu and Np. It was found that SNT can be formed at temperatures as low as 100 deg. C and short times. Samples were prepared at 200 deg. C hydrothermally as a function of time with the lowest time 1.5 h and the highest 27.5 h. Samples were also prepared at 170 deg. , 150 deg. , and 100 deg. for times ranging from 1 h to 20 h. Although the tests are not complete, in general it was found that the less crystalline the SNT the faster the kinetics of uptake. Furthermore, conversion of SNT to H+-SNT, i.e. replacement of Na+ by H+ increased the rate of uptake. These tests were carried out in 0.001 M Sr2+ at room temperature. Additional tests will be carried

out in the Savannah River simulant to determine the sample with the highest uptake and fastest kinetics. A sample will then be submitted to the WSRC laboratory for testing on the actual waste solutions.

CST: Crystalline Silicotitanate, Na2Ti2O3SiO4.2H2O. Two important discoveries were made during the course of our studies. 1. It was found that addition of small amounts of CsCl to the reactant mix decreased the amount of time to obtain crystalline CST from 10 days to one day. Furthermore, the uptake of Cs+ was small enough that all of it could be removed by washing with dilute (1M) HCl. This finding is also the case for the niobium containing CST. The implications of this discovery is that the time to prepare CST can be drastically reduced by templating with Cs+ with consequent cost savings. 2. It was found that rather than preparing the fully crystalline CST, lowering the temperature from 200 deg. C to 170 deg. C and reducing the time from 10 days to 3 days or less a poorly crystalline CST results. The removal of Sr2+ groundwater containing 600 mu g/L was determined using the poorly crystalline (P-CST) and the fully crystalline phases (CST). In the first minute the P-CST had removed 90% of the Sr2+ while the CST had removed only 60%. Furthermore, 100% removal was achieved by P-CST in 1 hr compared to 90% in 2 hr for the CST. We are in the process of preparing Nb-CST of low crystallinity to test for rate of Cs+ removal. Electron micrographs of the CST revealed the presence of rhombic crystals ranging in sizes of 0.3 to 3 mu in the long direction. In contrast the EM of P-CST revealed that it was a porous powder. Surface area measurements were determined by the sorption of N2 at 77 K for samples calcined at 150 deg. C and 210 deg. C. For P-CST the surface areas were 196 and 205 m2/g, respectively with no micropores. In contrast, the CST gave 86 m2/g with 11 m2/g due to micropores whereas the surface area decreased to 8.4 m2/g on heating to 210 deg. C with no micropores. We interpret these results to indicate that the P-CST exhibits faster kinetics because of its higher surface area. Even in this ill formed state the tunnels in P-CST must still be available for Cs+ uptake with a higher percentage open at the surface to accept Cs+. On the other hand the CST may go through a phase transition at 210 deg. C which drastically reduces its surface area.

In Situ Studies: In situ studies of CST crystallization were carried out at the NSLS at Brookhaven. A 5 mg gel of the correct ratio of reactants to form CST was placed inside a quartz capillary tube and heated to 210 deg. C. X-ray powder patterns were taken every 2.5 min. Analysis of the curves showed that almost immediately the SNT phase appeared. After four hours the major reflections for SNT began to decrease and the reflection for CST began to increase. The conversion of SNT to CST was complete in about one more hour. In subsequent ex-situ studies we found that perhaps 24-48 h are required for complete conversion of SNT to CST at 200 deg. C. By control of temperature and time it might be able to prepare a mixture of SNT and CST that would remove Cs, Sr and actinides from the Savannah River waste in one step. We are pursuing this goal. Also part of the in-situ studies is the determination of the mechanism of Cs+ ion exchange in CST. This study was carried out at room temperature. About 10 mg of crystalline CST in the H-form is held in a glass capillary tube by glass wool plugs. A solution of CsNO3 held at pH 11 with CsOH is allowed to flow through the open ended tube at the rate of one drop per minute. Our previous ex-situ work on the crystal structures showed that the H-form has unit cell dimensions of a = b = 11.039(1), c = 11.886(1) whereas the Cs+ phase has unit cell dimensions a = 7.826(1), c = 11.9815(4). The connection between the two unit cells is that the a-axis of the H-form is the diagonal of the ab square in the Cs+ form. The tunnel in the H-form is elliptical whereas in the Na+ or Cs+ it is more circular. Apparently the elliptical form allows the protons bonded to the cubane oxygens to readily hydrogen bond to the water molecules in the tunnel and the tunnel water molecules to be hydrogen donors to the framework oxygens. In the crystal structure of the Cs+ phase the Cs+ was located in two sites. Site-1 is in the tunnel at 1/4 c and 3/4 c and site-2 is also in the tunnel but at 0.13 c and 0.63 c. Approximately 80% of the Cs+ is in site 1 surrounded by eight framework oxygens to which it bonds. In site 2 the Cs+ is bonded to four framework oxygens and two water molecules. The mystery is why Cs+ should choose the less desirable site-2 at all. This mystery was resolved by the in-situ study. It turns out that site-2 is filled first and then site 1 begins to increase its occupancy. The reason is that the Cs+ cannot diffuse through the elliptical shaped part of the tunnel. The 1/4, 3/4 site is surrounded by 8-framework oxygens, four above and four below the site. The Cs+ is too large to enter site-1. Therefore, the lattice must vibrate and Cs+ passes through into site-1 converting the lattice back to a more symmetrical or circle-like shaped tunnel. The two sites are mutually exclusive, occupation of one must leave the other one adjacent to it empty. When the exchange is complete, some Cs+ always remains in site-2. In future in-situ work we will carry out similar ion exchange studies with Nb-CST, for Cs+ and Na+-Cs+ exchange rather than H+-Cs+ exchange. We will also begin work on

Sr2+ exchange in CST and Nb-CST. Most importantly we will study the crystal growth of Nb-CST to determine whether SNT also forms in this system.

Goals for the upcoming year

1. To optimize the crystallinity of both the CST and Nb-CST for maximum kinetic performance.
2. To optimize the preparation of SNT for maximum kinetic performance.
3. To establish the correct proportions of Nb-CST and SNT for the maximum removal of Cs+, Sr2+ and actinides in the shortest time for a single in-tank process to remove all the HLW to DOE standards.

DELIVERABLES: Publications 1. J.P. Larentzos, A. Clearfield, A. Tripathi, and E.J. Maginn, A Molecular Modeling Investigation of Cation and Water Siting in Crystalline Silicotitanates, J. Phys. Chem. B 108, 17560-17570 (2004). 2. A. Tripathi, D. G. Medvedev, and A. Clearfield, The Crystal Structures of Strontium Exchanged Sodium Titanosilicates in Relation to Selectivity for Nuclear Waste Treatment, J. Solid State Chem. 178, 253-261 (2005). 3. D. Medvedev, A. Tripathi, A. Clearfield, A. Celestian, J. Parise and J. Hanson, Crystallization of Sodium Titanium Silicate with Sitinakite Topology: Evolution from the Sodium Nonatitanate Phase, Chem. Mater. 16, 3659-3666 (2004). 4. A. Tripathi, D. Medvedev, J. Delgado, and A. Clearfield, Optimizing Cs-exchange in Titanosilicate with the Mineral Pharmacosiderite Topology: Framework Substitution of Nb and Ge, J. Solid State Chem., 177, 2903-2915 (2004).

Presentations

1. Presented lecture on "Crystal Structures of Titanosilicates: Complementing X-ray Powder Diffraction Techniques by Single Crystal Diffraction Methods" at the American Crystallographic Association Conference in Chicago, IL, July 16-20, 2004.

2. Presented lecture in India on "The Origin of Ion Exchange Selectivity in Framework Type Titanium Silicates" at the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore; presented lecture on "In Situ Study of Hydrothermally Prepared Titanates and Titanosilicates" at Sixth International Conference on Solvothermal Reactions, Mysore, Aug. 18-27, 2004.